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[54] **SEMICONDUCTOR APPARATUS UTILIZING
GRADIENT FREEZE AND LIQUID-SOLID
TECHNIQUES**

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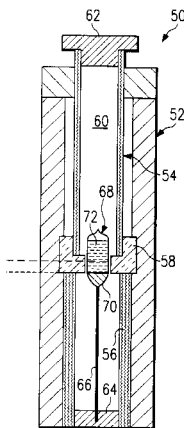
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[57] ABSTRACT

Transition metals of Group VIII (Co, Rh and Ir) have been prepared as semiconductor compounds with the general formula TSb₃. The skutterudite-type crystal lattice structure of these semiconductor compounds and their enhanced thermoelectric properties results in semiconductor materials which may be used in the fabrication of thermoelectric elements to substantially improve the efficiency of the resulting thermoelectric device. Semiconductor materials having the desired skutterudite-type crystal lattice structure may be prepared in accordance with the present invention by using vertical gradient freezing techniques and/or liquid phase sintering techniques. Measurements of electrical and thermal transport properties of selected semiconductor materials prepared in accordance with the present invention, demonstrated high Hall mobilities (up to 1200 cm².V⁻¹.s⁻¹) and good Seebeck coefficients (up to 150 μ VK⁻¹ between 300° C. and 700° C.). Optimizing the transport properties of semiconductor materials prepared from elemental mixtures Co, Rh, Ir and Sb resulted in a substantial increase in the thermoelectric figure of merit (ZT) at temperatures as high as 400° C. for thermoelectric elements fabricated from such semiconductor materials.

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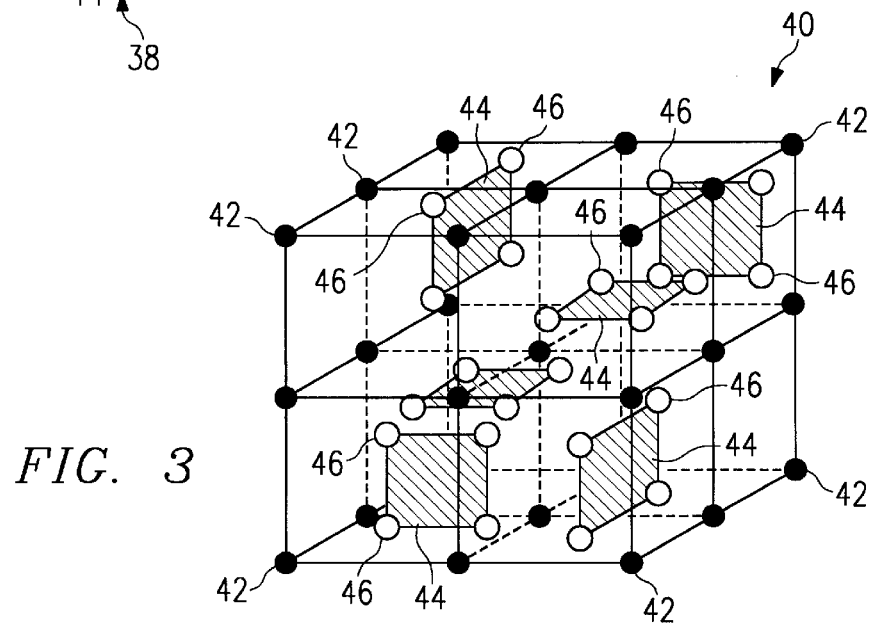
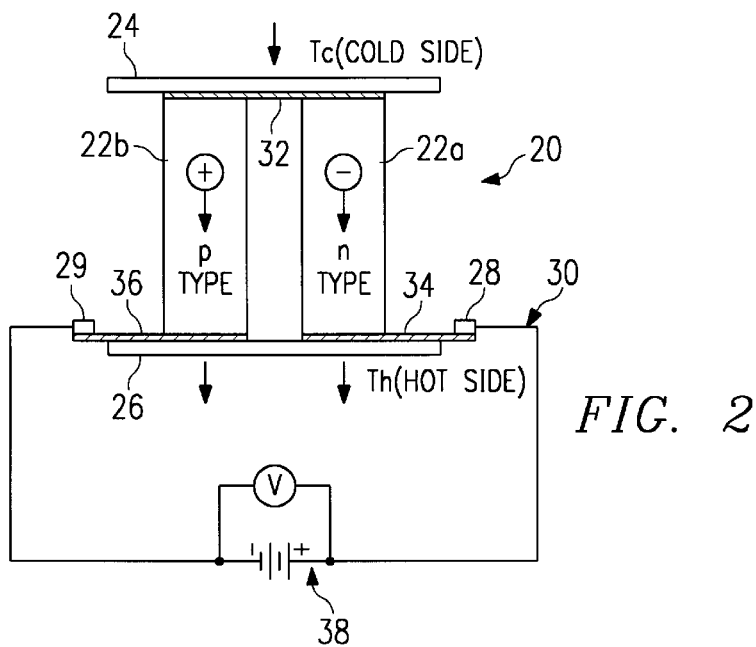
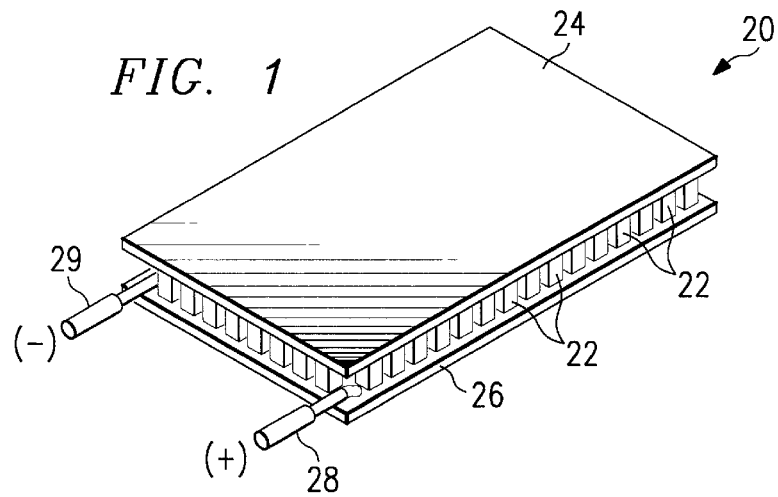
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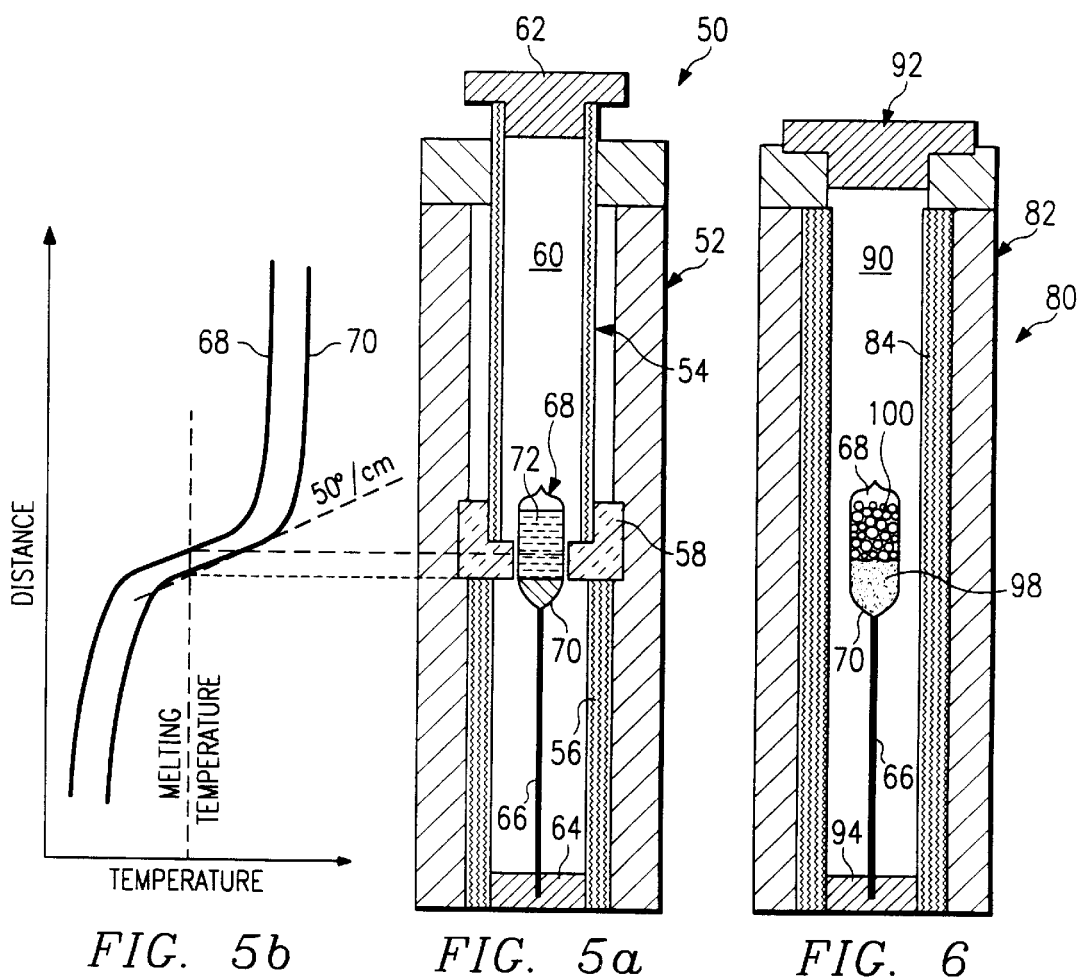
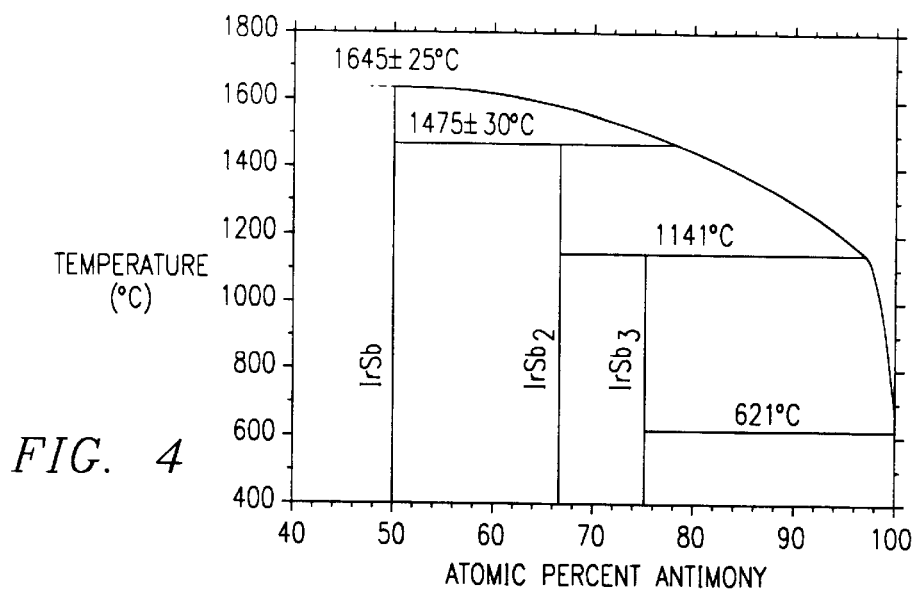
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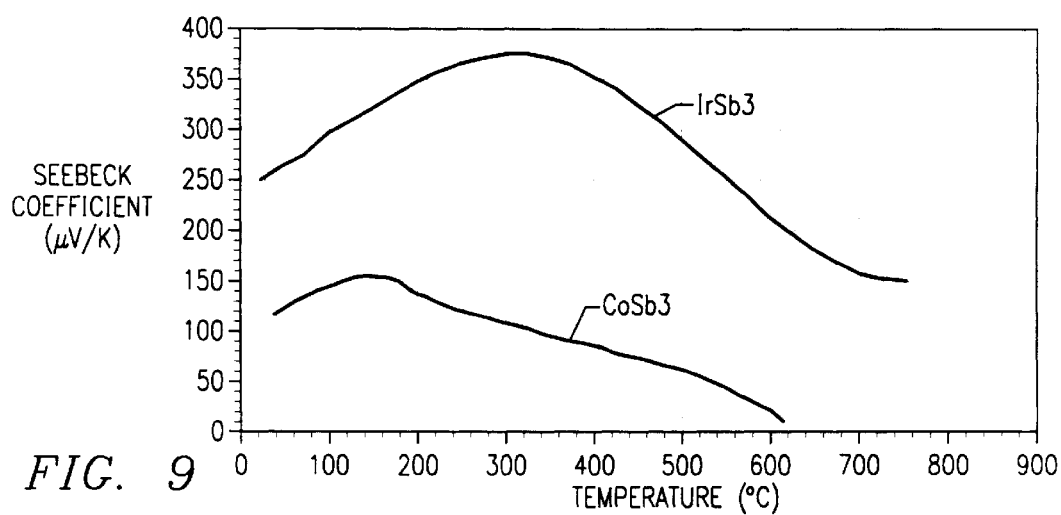
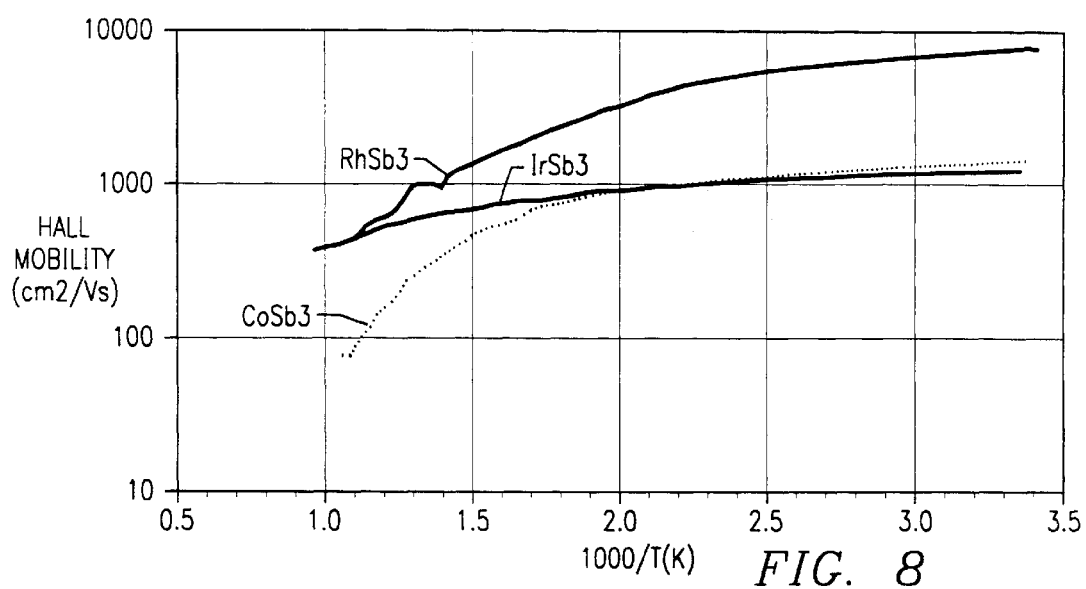
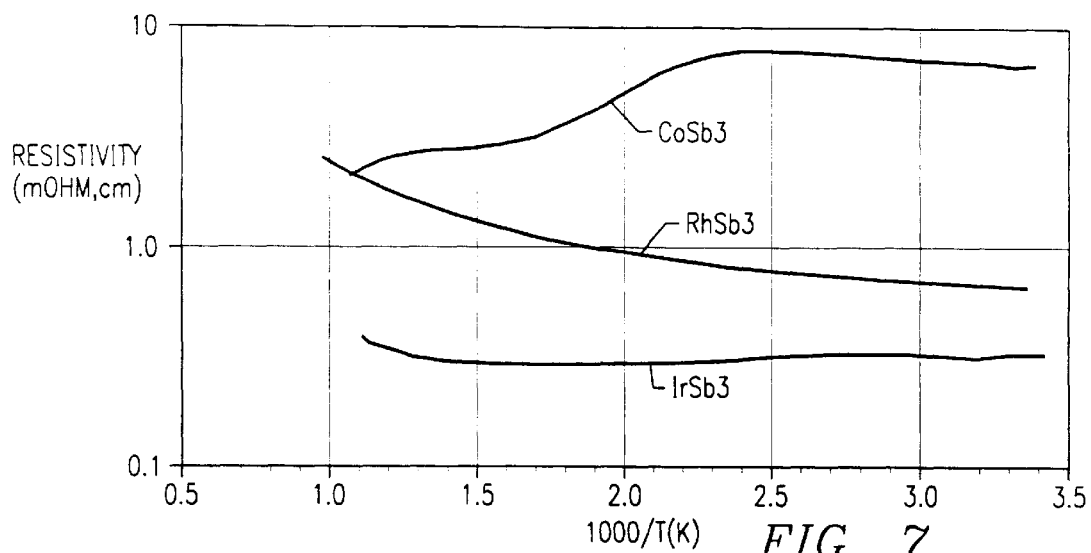
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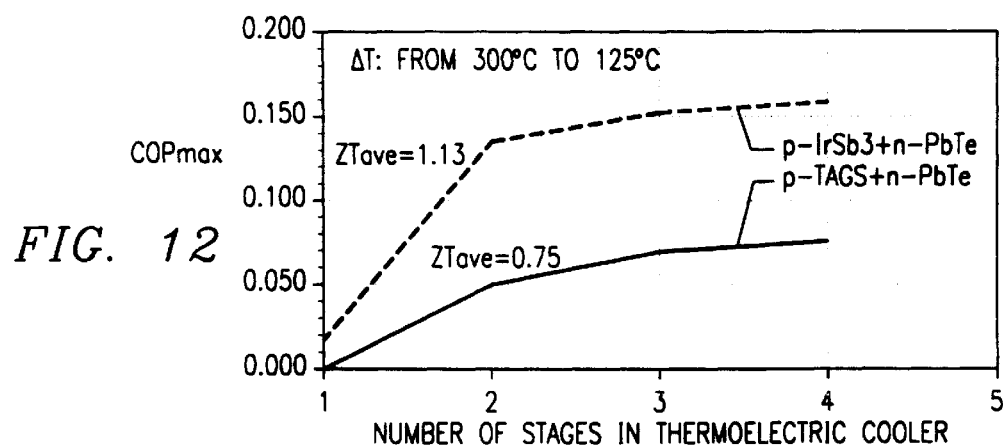
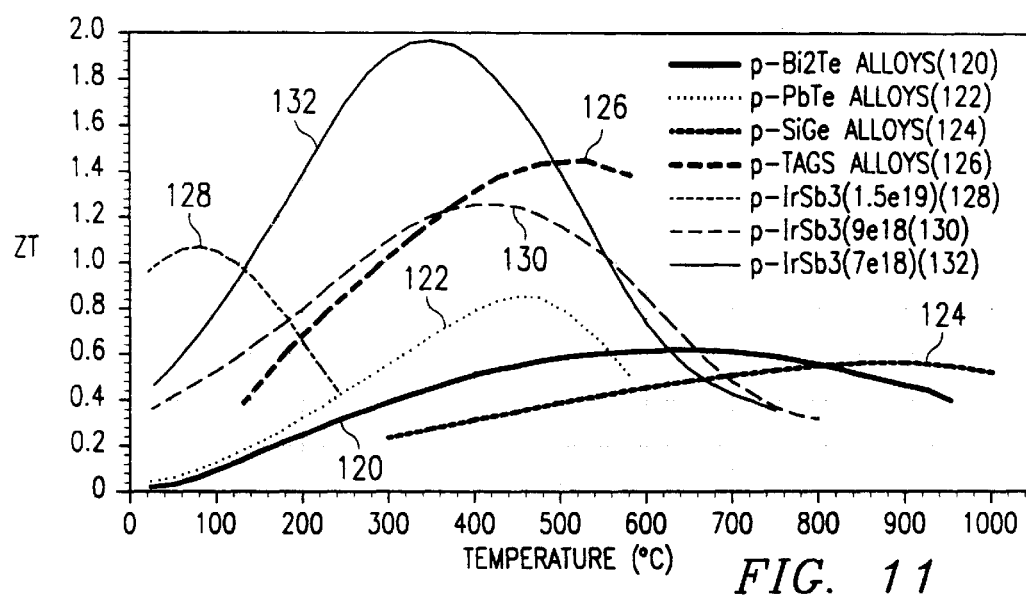
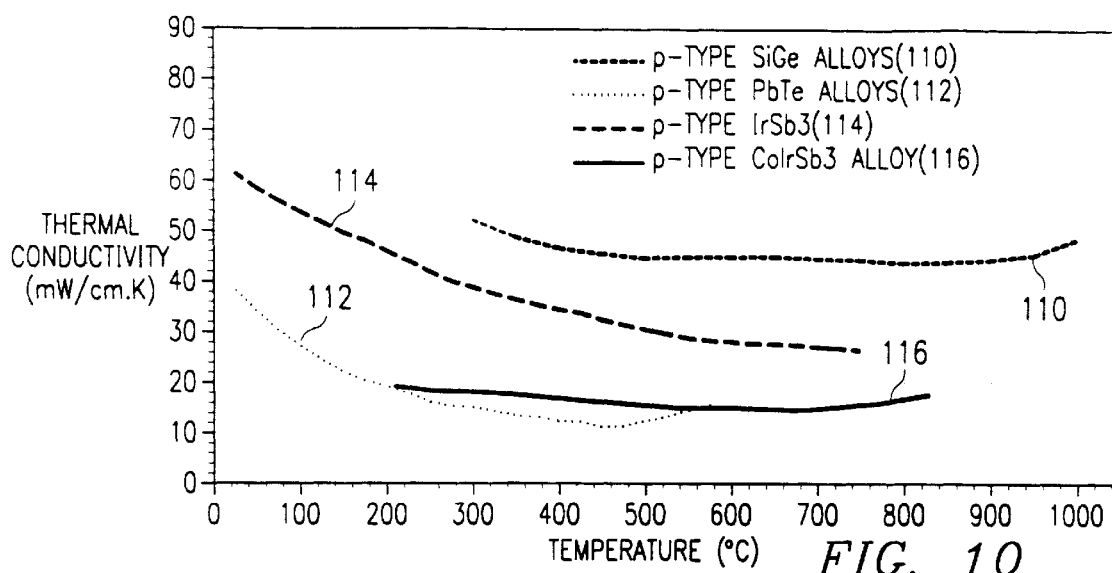
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SEMICONDUCTOR APPARATUS UTILIZING GRADIENT FREEZE AND LIQUID-SOLID TECHNIQUES

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the Contractor has elected to retain title.

TECHNICAL FIELD OF THE INVENTION

This invention relates to the design and preparation of semiconductor materials having enhanced thermoelectric properties.

BACKGROUND OF THE INVENTION

The basic theory and operation of thermoelectric devices has been developed for many years. Modern thermoelectric cooling devices typically include an array of thermocouples which operate by using the Peltier effect. Thermoelectric devices are essentially small heat pumps which follow the laws of thermodynamics in the same manner as mechanical heat pumps, refrigerators, or any other apparatus used to transfer heat energy. The principal difference is that thermoelectric devices function with solid state electrical components (thermocouples) as compared to more traditional mechanical/fluid heating and cooling components. The efficiency of a thermoelectric device is generally limited to its associated Carnot cycle efficiency reduced by a factor which is dependent upon the thermoelectric figure of merit (ZT) of the materials used in fabrication of the thermoelectric device.

The thermoelectric figure of merit (ZT) is a dimensionless measure of the effectiveness of a thermoelectric device and is related to material properties by the following equation:

$$ZT = S^2 \sigma T / \kappa \quad (1)$$

where S, σ , κ , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. The Seebeck coefficient (S) is a measure of how readily the respective carriers (electrons or holes) can change energy in a temperature gradient as they move across a thermoelectric element. The thermoelectric figure of merit is related to the strength of interaction of charge carriers with the lattice structure and the available energy states associated with the respective materials.

The ZT may also be stated by the equation:

$$ZT = \frac{S^2 T}{\rho \kappa} \quad (2)$$

ρ =electrical resistivity

σ =electrical conductivity

$$\text{electrical conductivity} = \frac{1}{\text{electrical resistivity}} \text{ or } \sigma = \frac{1}{\rho}$$

Thermoelectric materials such as alloys of Bi_2Te_3 , PbTe and BiSb were developed thirty to forty years ago. More recently, semiconductor alloys such as SiGe have been used in the fabrication of thermoelectric devices. Commercially available thermoelectric materials are generally limited to use in a temperature range between 300° K. and 1300° K. with a maximum ZT value of approximately one. The efficiency of such thermoelectric devices remains relatively low at approximately five to eight percent (5–8%) energy conversion efficiency. For the temperature range of –100° C.

to 1000° C., maximum ZT of current state of the art thermoelectric materials remains limited to values of approximately 1, except for Te-Ag-Ge-Sb alloys (TAGS) which may achieve a ZT of 1.2 to 1.4 in a very narrow temperature range. Recently developed materials such as $\text{Si}_{80}\text{Ge}_{20}$ alloys used in thermoelectric generators to power spacecrafts for deep space missions have a thermoelectric figure of merit approximately equal to 0.5 from 300° C. to 1,000° C.

SUMMARY OF THE INVENTION

In accordance with the present invention disadvantages and problems associated with the previous design and preparation of materials used in the manufacture of thermoelectric devices have been substantially reduced or eliminated. The present invention provides the ability to obtain increased efficiency from a thermoelectric device by using materials with a skutterudite-type crystal lattice structure and desired thermoelectric characteristics in fabrication of the thermoelectric device. Examples of semiconductor materials and compounds which are satisfactory for use with the present invention include, but are not limited to, IrSb_3 , RhSb_3 and CoSb_3 and alloys of these compounds.

In accordance with one aspect of the present invention, P-type semiconductor materials are formed from alloys of CoSb_3 , RhSb_3 or IrSb_3 for use in manufacturing thermoelectric devices with substantially enhanced operating characteristics and improved efficiency as compared to previous thermoelectric devices.

In accordance with another aspect of the present invention, N-type semiconductor materials are formed from alloys of CoSb_3 , RhSb_3 or IrSb_3 for use in manufacturing thermoelectric devices with substantially enhanced operating characteristics and improved efficiency as compared to previous thermoelectric devices.

An important technical advantage of the present invention includes the use of gradient freezing techniques in the preparation of semiconductor materials such as IrSb_3 , RhSb_3 and CoSb_3 . The use of gradient freezing techniques in accordance with the present invention produces a large, single crystal of semiconductor material having a skutterudite lattice structure. A Bridgman Two-Zone furnace and a sealed container have been modified for use in preparation of semiconductor materials in accordance with the present invention.

Another important technical advantage of the present invention includes the use of liquid phase sintering techniques in the preparation of semiconductor materials such as IrSb_3 , RhSb_3 and CoSb_3 . The use of liquid phase sintering techniques in accordance with the present invention produces a large, single crystal of semiconductor material having a skutterudite lattice structure. An isothermal furnace and a sealed container have been modified for use in preparation of semiconductor materials in accordance with the present invention.

Another aspect of the present invention includes manufacturing a thermoelectric device with P-type thermoelectric elements formed from materials such as CoSb_3 , RhSb_3 or IrSb_3 and N-type thermoelectric elements formed from $\text{Si}_{80}\text{Ge}_{20}$ or alloys of bismuth (Bi), arsenic (As), antimony (Sb), selenium (Se), and tellurium (Te), the salts of lead with chalconide materials, sulphur (S), tellurium and selenium.

The present invention allows the manufacture of thermoelectric energy conversion devices such as electrical power generators, coolers, and thermocouples or temperature detectors with high ZT and associated increased efficiency.

By the use of semiconductor compounds such as IrSb_3 , RhSb_3 and CoSb_3 and alloys of these compounds which have been prepared in accordance with the present invention, the overall efficiency of a thermoelectric device may be substantially enhanced. The thermoelectric elements or thermocouples fabricated from semiconductor materials such as IrSb_3 , RhSb_3 and CoSb_3 with skutterudite-type crystal lattice structures have demonstrated a ZT of 2 over a wide temperature range.

A further important technical advantage includes the use of semiconductor materials prepared in accordance with the present invention in the manufacture of a radioisotope thermoelectric generator (RTG) to substantially enhance the associated system efficiency and to significantly increase the operating temperature range of the resulting RTG. Such thermoelectric devices may be used in space power systems. Other thermoelectric devices manufactured from semiconductor materials fabricated in accordance with the present invention may be used in waste heat recovery systems, automobiles, remote power generators and sensors and coolers for advanced electronic components such as field effect transistors.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention and its advantages, reference is now made to the following description taken in conjunction with the accompanying drawings in which:

FIG. 1 is an isometric drawing of a thermoelectric device which may be manufactured from materials incorporating the present invention;

FIG. 2 is an electrical schematic drawing of the thermoelectric device of FIG. 1;

FIG. 3 is an isometric representation of a skutterudite-type crystal lattice structure associated with semiconductor materials which have been fabricated in accordance with the present invention;

FIG. 4 is an iridium antimony phase diagram;

FIG. 5a is a schematic drawing in elevation and in section with portions broken away showing a Bridgman Two-Zone furnace which may be used to prepare semiconductor materials using gradient freezing techniques in accordance with the present invention;

FIG. 5b is a graph showing the temperature gradient associated with growing large, single crystals of semiconductor materials having a skutterudite lattice structure in accordance with the present invention;

FIG. 6 is a schematic drawing in elevation and in section with portions broken away showing an isothermal furnace which may be used in growing large, single crystals of semiconductor materials having a skutterudite lattice structure in accordance with the present invention;

FIG. 7 is a graph showing typical electrical resistivity as an inverse function of temperature associated with semiconductor materials prepared in accordance with the present invention;

FIG. 8 is a graph showing typical Hall mobility values as an inverse function of temperature associated with semiconductor materials prepared in accordance with the present invention;

FIG. 9 is a graph showing typical Seebeck coefficients as a function of temperature for semiconductor materials prepared in accordance with the present invention;

FIG. 10 is a graph showing thermal conductivity as a function of temperature for semiconductor materials pre-

pared in accordance with the present invention as compared with presently available thermoelectric materials;

FIG. 11 is a graph showing the ZT as a function of temperature for P-type semiconductor materials prepared in accordance with the present invention having different doping levels as compared with the ZT of presently available P-type thermoelectric materials; and

FIG. 12 is a graph showing the performance of a multiple stage thermoelectric cooler fabricated in part from semiconductor materials incorporating the present invention as compared to a multiple stage thermoelectric cooler fabricated from presently available semiconductor materials.

DETAILED DESCRIPTION OF THE INVENTION

The preferred embodiments of the present invention and its advantages are best understood by reference to FIGS. 1 through 12 of the drawings, like numerals being used for like corresponding parts of the various drawings.

Thermoelectric device 20, as shown in FIGS. 1 and 2, may be manufactured from semiconductor materials and compounds which have been prepared in accordance with the present invention. The use of such semiconductor materials will substantially increase energy conversion efficiency. Thermoelectric device 20, as shown, may be used as a heater and/or a cooler. Thermoelectric device 20 is preferably manufactured with a plurality of thermoelectric elements (sometimes referred to as "thermocouples") 22 disposed between cold plate 24 and hot plate 26. Electrical power connections 28 and 29 are provided to allow attaching thermoelectric device 20 to an appropriate source of DC electrical power. If thermoelectric device 20 were redesigned to function as an electrical power generator, electrical connections 28 and 29 would represent the output terminals from such a power generator operating between hot and cold temperature sources (not shown).

FIG. 2 is a schematic representation of electrical circuit 30 associated with thermoelectric device 20. Electrical circuit 30 is also typical of electrical circuits associated with using thermoelectric elements or thermocouples to convert heat energy into electrical energy. Such electrical power generators may be used in waste heat recovery systems (not shown), space power systems (not shown) and radioisotope power generators (not shown).

Electrical circuit 30, which is typical for a single stage thermoelectric device such as thermoelectric device 20, generally includes two dissimilar materials such as N-type thermoelectric elements 22a and P-type thermoelectric elements 22b. Thermoelectric elements 22 are typically arranged in an alternating N-type element to P-type element configuration. In many thermoelectric devices, semiconductor materials with dissimilar characteristics are connected electrically in series and thermally in parallel.

N-type semiconductor materials have more electrons than necessary to complete a perfect molecular lattice structure. P-type semiconductor materials have fewer electrons than necessary to complete a lattice structure. The "missing electrons" are sometimes referred to as "holes." The extra electrons in the N-type semiconductor material and the holes in the P-type semiconductor material (hereinafter referred to as "carriers") are the agents which transport or move heat energy between cold side or cold plate 24 and hot side or hot plate 26 of thermoelectric elements 22. Ceramic materials are frequently used in the manufacture of plates 24 and 26 which define in part the cold side and hot side, respectively, of thermoelectric device 22.

In thermoelectric device **20**, alternating thermoelectric elements **22** of N-type and P-type semiconductor materials have their ends connected in a serpentine fashion by electrical conductors such as **32**, **34** and **36**. Conductors **32**, **34** and **36** are typically metalizations formed on the interior surfaces of plates **24** and **26**. Commercially available thermoelectric coolers may include two metalized ceramic plates with P-type and N-type elements of bismuth telluride alloys soldered between the ceramic plates.

When DC electrical power from power supply **38** is applied to thermoelectric device **20** having an array of thermoelectric elements **22**, heat energy is absorbed on cold side **24** of thermoelectric elements **22**. The heat energy passes through thermoelectric elements **22** and is dissipated on hot side **26**. A heat sink (sometimes referred to as the "hot sink", not shown) may be attached to hot plate **26** of thermoelectric device **20** to aid in dissipating heat from thermoelectric elements **22** to the adjacent environment. In a similar manner a heat sink (sometimes referred to as a "cold sink", not shown) may be attached to cold side **24** of thermoelectric device **20** to aid in removing heat from the adjacent environment. Thermoelectric device **20** may sometimes be referred to as a thermoelectric cooler. However, since thermoelectric devices are a type of heat pump, thermoelectric device **20** may function as either a cooler, heater, or power generator.

Semiconductor materials (sometimes referred to as "semiconductor compounds") CoSb_3 , RhSb_3 and IrSb_3 have been prepared in accordance with the present invention in the form of a large, single crystal with a skutterudite lattice structure **40** as shown in FIG. **3**. As will be explained later in more detail, such semiconductor materials are preferably prepared in an antimony rich environment. The skutterudite crystal lattice structure is defined in part by a unit cell with eight members having the formula AB_3 . A may be selected from the group consisting of Co, Rh and Ir. B may be Sb. The unit cell dimension is approximately 9.249 Angstroms. Alloys of these compounds having the formula $\text{Co}_{1-x-y}\text{Rh}_x\text{Ir}_y\text{Sb}_3$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$, have also been prepared using the present invention.

Skutterudite-type crystal lattice structure **40** includes a cubic lattice of metal atoms **42**. Metal atoms **42** are preferably selected from the group consisting of cobalt, iridium, and/or rhodium. A four-member planary ring **44** of non-metal atoms **46** is disposed within the cubic lattice structure. Planary rings **44** preferably include four atoms of antimony. Each metal atom **42** has six neighbor atoms **42**. Non-metal atoms **46** have two adjacent non-metal atoms **46** and two metal atoms **42**. The covalent bonding associated with skutterudite-type crystal lattice structure **40** provides high electron mobility and low thermal conductivity.

Semiconductor materials having skutterudite-type crystal lattice structure **40** may be doped with selected impurities to produce N-type thermoelectric elements **22a** and P-type thermoelectric elements **22b**. For example, adding platinum (Pt) as a doping agent with IrSb_3 semiconductor material produced N-type thermoelectric elements having a ZT of approximately two at a temperature of 400°C . If desired, thermoelectric device **20** may be manufactured with P-type thermoelectric elements **22b** fabricated from IrSb_3 and N-type thermoelectric elements **22a** fabricated from previously available semiconductor materials such as alloys of Bi, As, Sb, Te, salts of lead with chalcogenide materials, sulphur, tellurium and selenium.

Large, single crystals of semiconductor materials have been prepared in accordance with the present invention

using both gradient freezing techniques and liquid phase sintering techniques. The phase diagram for iridium-antimony, as shown in FIG. **4**, demonstrates that growth of the desired skutterudite-type crystal lattice structure is very difficult. Such crystal growth is preferably initiated from a narrow range of compositions. In addition, the liquid crystal curve in the region forming IrSb_3 is relatively sharp which further increases the difficulty of separating liquid and solid phases during crystallization.

Depending upon the type of semiconductor material and the relationship of cobalt, rhodium and iridium, either gradient freeze techniques or liquid phase sintering techniques may be used to produce the desired skutterudite-type crystal lattice structure. For some semiconductor materials such as CoSb_3 and RhSb_3 , gradient freeze techniques have produced the desired large, single crystal. For other semiconductor materials such as single phase IrSb_3 , liquid phase sintering techniques have produced the desired large, single crystals. Both methods of crystal growth, gradient freeze and liquid phase sintering, are preferably initiated from non-stoichiometric (antimony rich) melts based on the liquid phase diagram associated with the elements which will comprise the resulting semiconductor materials.

Large, single crystals of semiconductor materials with the desired skutterudite lattice structure **40** may be grown by using gradient freeze techniques and furnace **50** as shown in FIG. **5a**. Furnace **50** is frequently referred to as a Bridgman Two-Zone furnace. Furnace **50** includes housing **52** with a first or upper heater assembly **54** and a second or lower heater assembly **56**. Housing **52** defines in part chamber **60**. Thermal baffle **58** is preferably disposed between first heater assembly **54** and second heater assembly **56** intermediate chamber **60**. Various components which comprise furnace **50** are preferably disposed vertically within chamber **60** of housing **52**.

As shown in FIG. **5a**, housing **52** includes end closure **62** which seals the upper portion of chamber **60** and end closure **64** which seals the lower portion of chamber **60**. Quartz rod **66** may be vertically disposed within chamber **60**. Container **68** is preferably secured to one end of rod **66** adjacent to thermal baffle **58**.

The lower portion **70** of container **68** is preferably pointed or tapered with respect to rod **66**. Various types of containers **68** may be satisfactorily used with the present invention. A sealed quartz crystal or quartz ampoule has been found satisfactory for use with furnace **50**. If desired, housing **52** and end closure **64** may be modified to allow a conveyor (not shown) with a plurality of rods **66** and containers **68** to be passed sequentially through furnace **50**.

Elements such as Co, Rh and Sb powders which will be formed into the desired semiconductor material using furnace **50** are preferably sealed within container **68** under a vacuum. Pointed or tapered end **70** of container **68** is attached to quartz rod **66** and disposed vertically within chamber **60**. Tapered end **70** and its attachment to rod **66** cooperate to maintain the desired temperature gradients in container **68**. Furnace **50** is then heated to establish the temperature gradients **68** and **67** as shown in FIG. **5b**. Various temperature gradients may be used depending upon the elements placed within container **68** to produce the desired semiconductor material.

Samples of CoSb_3 and RhSb_3 were directionally crystallized from non-stoichiometric melts **72** rich in antimony. Crystals of CoSb_3 and RhSb_3 were grown with an axial temperature gradient of about $50^\circ\text{C}/\text{cm}$ and a growth rate about 1 mm/day. The crystals of CoSb_3 and RhSb_3 were approximately 10 mm long and 6 mm in diameter. The average density of the CoSb_3 crystals was measured and found to be 99.7% of the theoretical density ($7.69\text{ g}/\text{cm}^3$).

The average density of the RhSb_3 crystals was measured and found to be 99.5% of the theoretical density (7.69 g/cm^3). Crystals of the $\text{Ir}_x\text{Co}_{1-x}\text{Sb}_3$ solid solutions were also successfully grown by the gradient freeze technique from antimony-rich melts in furnace 50.

Large, single crystals of semiconductor materials with a skutterudite lattice structure may also be grown by using liquid phase sintering techniques and furnace 80 as shown in FIG. 6. Furnace 80 may be referred to as an isothermal furnace as compared to furnace 50 which has two different temperature zones. Furnace 80 includes housing 82 with heater assembly 84 disposed therein. Housing 82 defines in part chamber 90. Various components which comprise furnace 80 are preferably vertically disposed within chamber 90 of housing 82.

As shown in FIG. 6, housing 82 includes end closure 92 which seals the upper portion of chamber 90 and end closure 94 which seals the lower portion of chamber 90. Quartz rod 66 is preferably disposed vertically within chamber 90. Container 68 is preferably secured within chamber 90 intermediate end closures 94 and 92 at approximately the mid point of chamber 90.

The elements such as Ir, Rh, Co and Sb which will be used to form the desired semiconductor material may be sealed within container 68. The lower portion 70 of container 68 is preferably pointed or tapered with respect to quartz rod 66. The relationship of tapered end 70 with quartz rod 66 cooperate to maintain the desired temperature gradient in container 68 during growth of the skutterudite-type crystal structure 40. Various types of containers 68 may be satisfactorily used with the present invention. A sealed quartz crystal or crystal ampoule has been found satisfactory for use with the present invention. As previously noted for furnace 50, housing 82 and end closure 94 may be modified to allow a conveyor (not shown) to pass a plurality of rods 66 and containers 68 sequentially through furnace 80.

Liquid phase sintering techniques have been used to prepare large, single crystals of semiconductor material IrSb_3 and also some alloys of $(\text{Ir}_{1-x-y}\text{Rh}_x\text{Co}_y)\text{Sb}_3$ solid solutions using furnace 80 and container 68. The samples produced had good semiconducting properties including exceptional P-type Hall mobilities as high as $7725 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature. The crystals were approximately 10 mm long and 6 mm in diameter.

The liquid phase sintering technique used to produce IrSb_3 and $(\text{Ir}_{1-x-y}\text{Rh}_x\text{Co}_y)\text{Sb}_3$ solid solutions included placing a first layer 98 of elemental iridium, cobalt and/or rhodium powders together with a second layer 100 of antimony shots in a container sealed under vacuum. In the case of the preparation of a solid solution $(\text{Ir}_{1-x-y}\text{Rh}_x\text{Co}_y)\text{Sb}_3$, the powders of iridium, cobalt and rhodium in the desired amount were loaded in plastic vials, mixed and shaken in a mixer mill for about thirty minutes. The container 68 with material layers 98 and 100 was then held vertical and heated in furnace 80 as illustrated in FIG. 6. Several different reaction times and temperatures were tried. For some mixtures, the best results were obtained with a reaction time of 24 hours at a temperature of 1000°C . Under these conditions, the resulting crystals were the most dense.

Transport properties measurements performed on samples of CoSb_3 , RhSb_3 and $(\text{Ir}_{1-x-y}\text{Rh}_x\text{Co}_y)\text{Sb}_3$ prepared using the previously described procedures and apparatus demonstrated excellent semiconducting and thermoelectric properties. For example, the compounds with skutterudite crystallographic structure 40 had exceptional high P-type Hall mobilities. Room temperature values as high as $7725 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ were measured on a RhSb_3 sample at a doping level of $2.4 \cdot 10^{18} \text{ cm}^{-3}$. Although linked to the particular crystal structure of this compound, this high value is also a result of the good quality of the sample. For example, lower

mobilities were measured on hot-pressed RhSb_3 samples such as a maximum value of $1500 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. Mobility as high as $17321 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ were measured on P-type CoSb_3 single crystals compared to a maximum value of $290 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for samples prepared by other procedures. IrSb_3 samples also possessed high P-type Hall mobilities as high as $1241 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at a doping level of $7.2 \cdot 10^{18} \text{ cm}^{-3}$.

Semiconductor compounds and related solid solutions have also been prepared by sintering elemental powders of iridium, cobalt, rhodium and antimony in various ratios. Completion of the reaction was achieved in times as short as six hours at a temperature of 600°C . These powders have been successfully hot-pressed under specific conditions into large ingots (not shown).

Powders of IrSb_3 compound and several compositions of the $(\text{Ir}_{1-x-y}\text{Rh}_x\text{Co}_y)\text{Sb}_3$ solid solutions were also prepared in relatively short times (as low as six hours) by hot press sintering elemental powders or iridium, cobalt, antimony and rhodium. Several different mixtures of elemental powders were successfully hot-pressed in a graphite die (not shown) into dense ingots about 15 mm long and 6 mm in diameter. The resulting compounds demonstrated exceptional thermoelectric properties.

Doping of the elemental powders can be achieved by introducing the desired amount of dopant in the initial powder load. By using commercially available hot presses and graphite die containers, this process is quick, cost effective and may be easily adapted to industrial manufacturing of large quantities of $(\text{Ir}_{1-x-y}\text{Rh}_x\text{Co}_y)\text{Sb}_3$ samples of different compositions and doping level.

Semiconductor compounds of CoSb_3 , RhSb_3 and IrSb_3 with skutterudite-type crystal lattice structure prepared in accordance with the present invention have demonstrated the characteristics shown in the following Table 1.

TABLE I

Material	CoSb_3	RhSb_3	IrSb_3
Melting Point ($^\circ \text{C}$)	850	900	1140
Type of formation from the melt	peritectic	peritectic	peritectic
Structure type	cubic	cubic	cubic
Prototype	CoAs_3	CoAs_3	CoAs_3
Number of atoms/unit cell	32	32	32
Lattice parameter (\AA)	9.0347	9.2322	9.2533
Density ($\text{g} \cdot \text{cm}^{-3}$)	7.69	7.96	9.32
Thermal expansion coefficient ($^\circ \text{C}^{-1}$)			2×10^{-5}
Energy bandgap (eV)	0.5		1.17
Conductivity type	p	p	p
Electrical resistivity ($\text{m}\Omega \cdot \text{cm}$) at 25°C .	0.55	0.34	0.70
Hall mobility ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) at 25°C .	1732	7725	1241
Hall carrier concentration (cm^{-3}) at 25°C .	6.5×10^{18}	2.4×10^{18}	7.2×10^{18}
Seebeck coefficient ($\mu\text{V} \cdot \text{K}^{-1}$ at 25°C .	150		250

FIG. 7 is a graphical representation of typical electrical resistivity values as a function of inverse temperature for semiconductor compounds CoSb_3 , RhSb_3 and IrSb_3 having skutterudite-type crystal lattice structure 40. FIG. 8 is a graphical representation of typical Hall mobility functions as a measure of inverse temperatures for semiconductor compounds CoSb_3 , RhSb_3 and IrSb_3 having skutterudite-type crystal lattice structure 40. FIG. 9 is a graphic representation

of typical Seebeck coefficient values as a function of temperature for semiconductor compounds CoSb_3 and IrSb_3 having skutterudite-type crystal lattice structure 40.

FIG. 10 comparisons of thermal conductivity as a function of temperature for semiconductor materials IrSb_3 and $\text{Ir}_{0.5}\text{Co}_{0.25}\text{Sb}_3$ prepared in accordance with the present invention as compared with previously available thermoelectric materials SiGe alloys and PbTe alloys. Curves 110 and 112 show thermal conductivity measured for semiconductor materials SiGe and PbTe respectively. Curves 114 and 116 are based on thermal conductivity measurements for semiconductor materials IrSb_3 and $\text{Ir}_{0.75}\text{Co}_{0.25}\text{Sb}_3$ respectively. FIG. 11 is a graph showing various values of thermoelectric ZT as a function of temperature for various samples of semiconductor material IrSb_3 with different doping levels. FIG. 11 also contains a graphical representation of ZT for previously available P-type thermoelectric materials. As previously noted, platinum has been found to be a satisfactory doping impurity for use with semiconductor materials having a skutterudite lattice structure 40.

A multiple stage thermoelectric cooler (not shown) is typically fabricated by vertically stacking two or more single stage thermoelectric devices 20. Each ascending thermoelectric device will have fewer thermoelectric elements or thermocouples 22. A multiple stage thermoelectric cooler is therefore typically pyramid shaped because the lower stage requires more thermoelectric elements to transfer the heat dissipated from the upper stage in addition to the heat pumped from the object being cooled by the multiple stage thermoelectric cooler. Field effect transistors are often cooled from 300° C. to 125° C. by using such multiple stage thermoelectric coolers.

P-type semiconductor material IrSb_3 prepared in accordance with the present invention may be used to provide a portion of thermoelectric elements 22. Currently available N-type semiconductor materials Bi_2Te_3 may be used to provide another portion of thermoelectric elements 22. The resulting combination substantially enhances the performance of thermoelectric device 20. This combination of P-type and N-type semiconductor materials is particularly useful in the 100° C. to 400° C. temperature range. FIG. 12 is a graphical representation showing the increase in multiple stage thermoelectric cooler performance resulting from the use of P-type semiconductor materials IrSb_3 . FIG. 12 shows the coefficient of performance (COP_{MAX}) as a function of the number of stages in each thermoelectric cooler.

Although the present invention has been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and the scope of the invention as defined in the following claims.

What is claimed is:

1. An apparatus using a gradient freeze technique to prepare a semiconductor alloy for use in fabricating thermoelectric elements comprising:

- a furnace defined in part by a housing having a chamber with a first heater and a second heater disposed therein;
- the first heater disposed within the chamber above the second heater;
- a thermal baffle disposed within the chamber between the first heater and the second heater;
- a container disposed within the chamber with the container adjacent to the thermal baffle;
- the container sealed with a vacuum formed therein;
- a rod vertically disposed within the chamber and the container secured to one end of the rod; and
- a plurality of elemental materials selected from the group comprising Co, Rh, Ir and Sb disposed within the

container for melting within the furnace to form the semiconductor alloy.

2. The apparatus as defined in claim 1 wherein the container further comprises a sealed quartz ampoule having a pointed end for attachment to the rod.

3. The apparatus as defined in claim 1 wherein the container further comprises:

- a sealed vessel with a first elemental material and a second elemental material; and

- the first elemental material selected from the group consisting of iridium, rhodium and cobalt, and the second elemental material comprising antimony.

4. The apparatus as defined in claim 3, further comprising an atomic ratio of antimony as compared to the first elemental material greater than 8 to 1.

5. The apparatus as defined in claim 1 further comprising the first heater, the second heater, and the thermal baffle cooperating to form a sharp temperature gradient within the container to form a single crystal of semiconductor alloy selected from the group consisting of CoSb_3 , RhSb_3 and $\text{Co}_{1-x-y}\text{Rh}_x\text{Ir}_y\text{Sb}_3$ wherein $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

6. The apparatus of claim 1 wherein the elemental materials comprise an antimony rich melt.

7. An apparatus using a liquid-solid phase sintering technique to prepare a semiconductor alloy for use in fabricating thermoelectric elements comprising:

- an isothermal furnace defined in part by a housing having a chamber with a heater disposed therein;

- a container disposed within the chamber, with the container spaced intermediate from the interior surfaces of the chamber; and

- a stoichiometric mixture of elemental materials selected from the group consisting of Co, Rh, Ir and Sb disposed within the container for melting within the furnace to form the desired semiconductor alloy.

8. The apparatus as defined in claim 7 wherein the container further comprises a sealed quartz ampoule having a pointed end for attachment to the rod.

9. The apparatus as defined in claim 7 further comprising:

- a layer of iridium powder disposed within the lower portion of the container adjacent to the rod; and

- a layer of antimony disposed within the container above the iridium powder.

10. The apparatus as defined in claim 7 wherein the container further comprises:

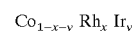
- a sealed vessel with a first elemental material layer and a second elemental material layer;

- the first elemental material layer disposed within the lower portion of the sealed vessel, and the second elemental material layer disposed above the first material layer; and

- the first elemental material layer selected from the group consisting of iridium, rhodium and cobalt, and the second elemental material layer comprising antimony.

11. The apparatus as defined in claim 10, further comprising an atomic ratio of antimony in the second material layer as compared to material in the first layer greater than 8 to 1.

12. The apparatus as defined in claim 10 wherein the first material comprises a mixture of:



wherein $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

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